VIVEKANANDA COLLEGE
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NAAC ACCREDITED ‘A’ GRADE

Topic:	Non Ideal Solutions
Course Title:	General Physical Chemistry
Paper:	BCMA CC3
Unit:	Non Ideal Solutions and Thermodynamics of EMF of cells
Semester:	2
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Name of the Department:	Biochemistry

- Gas-ion half cell:

eg. hydrogen gas-hydrogen ion ½ cell
Purified $H_2(g)$ passed over Pt electrode dipped in an acidic solution

$$H^+(aq) + e^-(Pt) \rightleftharpoons \frac{1}{2} H_2(g)$$

$$E_{H^+|H_2|Pt} = E^0_{H^+|H_2|Pt} - \frac{RT}{F} \ln \frac{(f_{H_2(g)}/f^0)^{1/2}}{a_{H^+}} \quad [n=1]$$

- Metal-metal ion half cell:

Consists of a metal electrode dipped in a solution of M^{n+} ions.
eg $Zn - Zn^{2+}$, $Cu - Cu^{2+}$, etc.

$$M^{n+}(aq) + ne^- \rightleftharpoons M(s)$$

$$E_{M^{n+}/M} = E^0_{M^{n+}/M} - \frac{RT}{nF} \ln \frac{1}{a_{M^{n+}}} \quad [a_{M(s)} = 1]$$

- Cell Reactions:

$$Zn | Zn^{2+} || Cu^{2+} | Cu$$

LH ½ cell: $Zn \rightarrow Zn^{2+} + 2e^-$ $\quad E_{Zn^{2+}/Zn} = E^0_{Zn^{2+}/Zn} - \frac{RT}{2F} \ln \frac{1}{a_{Zn^{2+}}}$

RH ½ cell: $Cu^{2+} + 2e^- \rightarrow Cu$ $\quad E_{Cu^{2+}/Cu} = E^0_{Cu^{2+}/Cu} - \frac{RT}{2F} \ln \frac{1}{a_{Cu^{2+}}}$

Adding, $Zn + Cu^{2+} \rightleftharpoons Zn^{2+} + Cu$

$$E_{cell_1} = E_R - E_L$$

$$= E_{Cu^{2+}|Cu} - E_{Zn^{2+}|Zn}$$

$$= \left[E^0_{Cu^{2+}|Cu} - E^0_{Zn^{2+}|Zn}\right] - \frac{RT}{2F} \ln \frac{a_{Zn^{2+}}}{a_{Cu^{2+}}}$$

$$\Rightarrow \boxed{E_{cell_1} = E^0_{cell_1} - \frac{RT}{2F} \ln \frac{a_{Zn^{2+}}}{a_{Cu^{2+}}}}$$

For the cell, $Cu|Cu^{2+}||Zn^{2+}|Zn$,

$$\boxed{E_{cell_2} = E^0_{cell_2} - \frac{RT}{2F} \ln \frac{a_{Cu^{2+}}}{a_{Zn^{2+}}}}$$

Obviously, $E_{cell_2} = -E_{cell_1}$

and cell reaction = Reduction at RHE - Oxidation at LHE

Generally,

$$E_{cell} = E^0_{cell} - \frac{RT}{nF} \ln \left\{ \prod_i (a_i)^{\nu_i} \right\}$$

$n \rightarrow$ no. of e^- involved

$\nu_i \rightarrow$ stoichiometry of the species

and $E^0_{cell} = E^0_R - E^0_L$

$\downarrow$

standard reduction potential

The amount of work involved in moving n no. of electrons from the left hand half cell to the right hand half cell is

$$W = -nF[E_R - E_L] = -nF E_{cell},$$

where $F = 96500 \ C\,mol^{-1}$ (Faraday)

and $\Delta G = -nFE_{cell}$

i.e. ΔG and E_{cell} have opposite signs.

ΔG	E_{cell}	Nature of reaction
$\ominus$	$\oplus$	Spontaneous
$\oplus$	$\ominus$	Non-spontaneous
0	0	Equilibrium

⇒ For the general rxn : $M^{n+} + ne^- \rightleftharpoons M$

$$E_{M^{n+}/M} = E^0_{M^{n+}/M} - \frac{RT}{nF} \ln \frac{1}{a_{M^{n+}}}$$

i.e. $E_{M^{n+}/M}$ increases as $a_{M^{n+}}$ increases & vice-versa.

→ For 10 times decrease in $a_{M^{n+}}$, there is $\frac{0.0592}{n}$ volt decrease in the reduction potential.

For $n=1$, E decreases by 0.0592 V for 10 times decrease in $a_{M^{n+}}$.

$n=2$, E decreases by $\frac{0.0592}{2}$ V or 0.0296 V

⇒ Determination of thermodynamic data:

$$\Delta G = -nFE_{cell} \Rightarrow \left[\frac{\partial(\Delta G)}{\partial T}\right]_P = -nF\left(\frac{\partial E}{\partial T}\right)_P$$

↓ Temp. coeff. of E

Again, from Gibbs Helmontz eq.

$$\Delta G = \Delta H + T\left(\frac{\partial \Delta G}{\partial T}\right)_P$$

$$\Rightarrow -nFE = \Delta H - nFT\left(\frac{\partial E}{\partial T}\right)_P$$

$$\Rightarrow \Delta H = -nF\left[E - T\left(\frac{\partial E}{\partial T}\right)_P\right] \quad (1)$$

Unit of ΔH : volt - coulomb [same as joule unit]

$$\Delta G = \Delta H - T\Delta S$$

$$\Rightarrow \Delta S = \frac{\Delta H - \Delta G}{T} = nF\left(\frac{\partial E}{\partial T}\right)_P \quad (2)$$

$$\Delta G^\circ = -RT \ln K^\circ_{eq} = -nFE^\circ_{cell}$$ [under standard conditions]

$$\Rightarrow E^\circ_{cell} = \frac{RT}{nF}\ln K^\circ_{eq} = \frac{2.303\,RT}{nF}\log K^\circ_{eq} \quad (3)$$

At 298K,

$$E^\circ_{cell} = \left(\frac{0.0592\,V}{n}\right)\log K^\circ_{eq} \quad (4)$$

⇒ Glass electrode:

Consists of a special glass tube of relatively low melting point and high electrical conductance.
The bulb contains a solution of constant H^+ ion concentration and an electrode of definite potential.
Usually, Ag-AgCl electrode dipped in 0.1 mol dm^{-3} HCl solution or a Pt wire inserted in a pH 4.0 buffer containing a small quantity of quinhydrone.
The bulb is inserted into a solution whose pH is to be determined.

$$Ag \mid AgCl(s) \mid 0.1 \text{ mol dm}^{-3}\ KCl \mid Glass \mid \text{Solution of unknown pH} \mid Calomel$$

$$E_{cell} = E_R - E_L$$

E_R ↓ Reduction potential of ref. electrode

$$E_L \equiv Ag \mid AgCl \mid 0.1 \text{ mol dm}^{-3}\ HCl \mid Glass \mid \text{Experimental solution of unknown pH}$$

$$E_{glass} = E^\circ_{glass} - \frac{RT}{F} \ln a_{H^+}$$

a_{H^+} → activity of H ions in experimental solution

$$\boxed{E_{glass} = E^\circ_{glass} + \frac{2.303RT}{F} pH}$$

$$E_{cell} = E_{calomel} - E_{glass}$$

$$= E_{calomel} - E^\circ_{glass} - \frac{2.303RT}{F} pH$$

At pH = 7, $E^\circ_{glass} = 0.062$ V

Components : (Tube within a tube)

A bulb ~~of~~ made from a specific glass

internal electrode Ag/AgCl or calomel

internal solution pH = 7 of 0.1 mol dm^{-3} KCl

reference electrode (same as internal electrode)

reference solution (0.1 mol/L KCl)

Inner tube contains an unchanging 1×10^{-7} mol dm^{-3} HCl solution.

$Ag(s) \mid AgCl(s) \mid KCl(aq) \parallel 1\times10^{-7} M\ H^+ \parallel$ glass $\parallel$ test solution $\parallel$ junction $\parallel KCl(aq) \mid AgCl(s) \mid Ag(s)$

→ $Ox + ne^- \rightleftharpoons Red$

$\Delta G = \Delta G^\circ + RT \ln Q$ Q → reaction quotient

$\Delta G^\circ = -nFE^\circ$ and $\Delta G = -nFE$

⇒ $-nFE = -nFE^\circ + RT \ln Q$

⇒ $E = E^\circ - \frac{RT}{nF} \ln Q = E^\circ - \frac{RT \times 2.303}{nF} \log Q$

⇒ $$\boxed{E = E^\circ - \frac{0.0592}{n} \log Q}$$

eg $A + ne^- \rightleftharpoons A^{n-}$ $E = E^\circ - \frac{RT}{nF} \ln \frac{[A^{n-}]}{[A]}$